

PTO 05-299

Chinese Patent

CN 1398923A

MODIFIED MICROFINE ZINC OXIDE AND ITS PREPARATION

[Gaixing De Chaoxi Yanghuaxin Jiqi Zhibei Fangfa]

Luo Tianrong, Zhao Yonghong, Guo Jianping, Qiao Aiping, Jiang Suping

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D. C. October 2004

Translated by: Schreiber Translations, Inc.

Country : People's Republic of China

Document No. : 1,398,923

Document Type : Patent

Language : Chinese

Inventor : Luo Tianrong, Zhao Yonghong, Guo
Jianping, Qiao Aiping, Jiang Suping

Applicant : Luo Tianrong

IPC : C09C 1/04, C01G 9/02, C04B 35/453, C04B
35/642, C08K 3/22

Application Date : January 30, 2002

Publication Date : February 26, 2003

Foreign Language Title : Gaixing De Chaoxi Yanghuaxin Jiqi
Zhifei Fangfa

English Title : MODIFIED MICROFINE ZINC OXIDE AND ITS
PREPARATION

[57] Abstract

This invention concerns a modified nanometer and sub-micron microfine zinc oxide and its preparation, which belongs to nanometer material production technique. The modified microfine zinc oxide is obtained by adding modifying solvent such as surface modifier, new polymer super dispersant, or amphoteric coupling agent in the zinc oxide prepared from ammonia evaporation process of alkaline preparation, and by applying appropriate modification process and method. This method takes advantage of the space steric effect of surface active agent to effectively control the size of zinc oxide so as to obtain good dispersivity and highly functional modified microfine zinc oxide. This preparation method is cost-effective, practical, and easy to operate. The modified microfine zinc oxide powder can be broadly applied in rubber, ceramic, textile, and general chemical industries.

¹ Numbers in the margin indicate pagination in the foreign text.

Claims

This invention involves in:

1. This invention concerns a modified microfine zinc oxide, which is nanometer and sub-micron microfine zinc oxide. In the ammonia evaporation process for the alkaline preparation of microfine zinc oxide or/and after preparation of microfine zinc oxide, modifying solvent is added in the zinc oxide and appropriate modification process and method are applied to modify microfine zinc oxide in order to obtain high performance, multi-functional, modified nanometer and sub-micron microfine zinc oxide. The modifying solvent added in the modification preparation process can be surface modifier, or new polymer super dispersant, or amphoteric coupling agent. The amount of each modifying solvent added is 0.1~20% of the content of zinc oxide (in weight proportion).

2. A modified microfine zinc oxide as described in Claim 1, whereas the modifying solvent added in the modification preparation is one of two kinds of the following modifying solvents, whereas the amount of each modifying solvent added or the total amount of two kinds of modifying solvents added accounts for 0.1~20% of the content

of zinc oxide (in weight proportion);

a. The surface active agent of modifying solvent added in the modification preparation process is anion surface active agent and non-ionic surface active agent, whereas the anion surface active agent includes C_{12-18} aliphatic acid and its salt, alkylbenzene sulfonate, alkyl ether organic phosphate, and alcohol ether carboxylate, whereas non-ionic surface active agent includes polyethylene (the molecular weight is $\overline{M}=200-20000$) and fatty alcohol polyoxyethylene ether;

b. The new polymer super dispersant of modifying solvent added in the modification preparation process is polyacrylate, and water soluble and oil soluble silicon oil;

c. The amphoteric coupling agent of modifying solvent added in the modification preparation process is silane coupler, titanate coupler, and aluminate coupler, whereas titanate coupler includes water soluble and oil soluble titanate coupler.

3. A modified microfine zinc oxide as described in Claim 2, whereas:

/3

a. The added amount of ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, or alcohol ether carboxylate ($0.1\sim 1\text{mol/L}$) serving as the said anion surface active agent is $0.5\sim 15\%$ (in weight proportion) of the content of zinc oxide

in zinc-ammonia complex solution, while the added amount of stearic acid (0.1~1mol/L) is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; The added amount of polyethylene or fatty alcohol polyoxyethylene ether (0.1~1mol/L) serving as non-ionic surface active agent is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution;

b. The said polyacrylate serving as a polymer super dispersant is a water solvent prepared in the following ratio: polyacrylate: water = 1: 10~100 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The water soluble silicon oil is prepared in the following ratio: water soluble silicon oil: water = 1: 10~100 (in weight proportion). The oil soluble silicon oil is prepared in the following ratio: oil soluble silicon oil: alcohol = 1: 10~100 (in weight proportion). The added amount of both solvents is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution.

c. The said amphoteric coupling agent includes oil soluble and water soluble titanate coupler, or water soluble silane coupler, or water soluble aluminate coupler. The water soluble titanate coupler,

or water soluble silane coupler, or aluminate coupler is prepared in the following ratio: water soluble titanate, or water soluble silane, or aluminate: water = 1: 1~2- (in weight proportion). The added amount of the solvent is 2~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The oil soluble titanate coupler is prepared in the following ratio: oil soluble titanate: alcohol = 1: 1~20 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution.

4. A method for the preparation of modified microfine zinc oxide, especially the preparation of nanometer and sub-micron modified microfine zinc oxide by adding modifying solvent during the ammonia evaporation process of alkaline preparation of microfine zinc oxide or/and in the prepared microfine zinc oxide. This preparation method enables microfine zinc oxide to alter its properties, improve or enhance its functionality. In the said preparation method, the added modifying solve is surface active agent, or new polymer super dispersant, or amphoteric coupling agent;

/4

The method for the preparation of modified microfine zinc oxide includes operating steps and processes of wet preparation, dry preparation, or wet-dry combined preparation, whereas:

a. The operating steps and processes of wet preparation of modified microfine zinc oxide include:

(1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use;

(2) In the ammonia evaporation process of alkaline preparation of microfine zinc oxide, add water soluble or oil soluble modifying solvent at normal temperature and pressure in the zinc-ammonia complex solution in the ammonia evaporation equipment in the amount of 0.1~20% (in weight proportion) of content of zinc oxide in zinc-ammonia complex solution, and then stir the solution, increase temperature, evaporate ammonia, stop ammonia evaporation when the ammonia content in the solution is less than 5% (in weight proportion), and conduct follow-up processes to obtain modified microfine zinc oxide powder to test and store for later use;

b. The operating steps and processes of dry preparation of modified microfine zinc oxide include:

(1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use;

(2) Place microfine zinc oxide powder made from alkaline

preparation process in the preparation equipment. Stir, increase temperature, and add water soluble modifying solvent. Increase temperature to 100~110°C. Upon finishing addition of modifying solvent, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. The amount of added modifying solvent is 0.1~20% (in weight proportion) of the content of zinc oxide. While adding oil soluble modifying solvent, it is necessary to stir dry zinc oxide powder in the preparation equipment, increase temperature and add oil soluble modifying solvent. Upon finishing addition of modifying solvent, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. The amount of modifying solvent added is 0.1~20% (in weight proportion) of the content of zinc oxide;

(3) Take out the modified microfine zinc oxide powder obtained from dry preparation to test and store for later use;

c. The operating steps and processes of wet-dry combined preparation of modified microfine zinc oxide include: 5

(1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use; The total amount of one modifying solvent added in two times or two modifying solvents altogether is 0.1~20% of the content of zinc oxide.

(2) In the ammonia evaporation process of alkaline preparation of microfine zinc oxide, add water soluble or oil soluble modifying solvent at normal temperature and pressure in the zinc-ammonia complex solution in the ammonia evaporation equipment, stir the solution, increase temperature, evaporate ammonia, stop ammonia evaporation when the ammonia content in the solution is less than 5% (in weight proportion), and then conduct follow-up processes to obtain modified microfine zinc oxide powder. After that, apply dry preparation method.

(3) Take modified microfine zinc oxide powder obtained from wet preparation and place the modified zinc oxide dry powder in the preparation equipment. Stir the solution, increase temperature, and add in water soluble modifying solvent. When the temperature increases to 100~110°C, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. While adding oil soluble modifying solvent, it is necessary to first stir the dry zinc oxide powder in the preparation equipment, increase temperature, and add in oil soluble modifying solvent. Upon finishing addition of modifying solvent, keep the temperature constant and stir zinc oxide powder for 30~60 minutes;

(4) Take out the modified microfine zinc oxide powder prepared through wet-dry combine methods to test and store for later use;

5. A method for the preparation of modified microfine zinc oxide

as described in Claim 4, whereas the modifying solvent added in the modification preparation is one of two kinds of the following modifying solvents, whereas the amount of each modifying solvent added or the total amount of two kinds of modifying solvents added accounts for 0.1~20% of the content of zinc oxide (in weight proportion);

a. The surface active agent of modifying solvent added in the modification preparation process is anion surface active agent and non-ionic surface active agent, whereas the anion surface active agent includes C_{12-18} aliphatic acid and its salt, alkylbenzene sulfonate, alkyl ether organic phosphate, and alcohol ether carboxylate, whereas non-ionic surface active agent includes polyethylene (the molecular weight is $\overline{M}=200-20000$) and fatty alcohol polyoxyethylene ether;

b. The new polymer super dispersant of modifying solvent added in the modification preparation process is polyacrylate, and water soluble and oil soluble silicon oil;

/6

c. The amphoteric coupling agent of modifying solvent added in the modification preparation process is silane coupler, titanate coupler, and aluminate coupler, whereas titanate coupler includes water soluble and oil soluble titanate coupler.

6. A method for the preparation of modified microfine zinc oxide as described in Claim 5, whereas:

a. The added amount of ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, and alcohol ether carboxylate (0.1~1mol/L) serving as the said anion surface active agent is 0.5~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution, while the added amount of stearic acid (0.1~1mol/L) is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; The added amount of polyethylene or fatty alcohol polyoxyethylene ether (0.1~1mol/L) serving as non-ionic surface active agent is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution;

b. The said polyacrylate serving as a polymer super dispersant is a water solvent prepared in the following ratio: polyacrylate: water = 1: 10~100 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The water soluble silicon oil is prepared in the following ratio: water soluble silicon oil: water = 1: 10~100 (in weight proportion). The oil soluble silicon oil is prepared in the following ratio: oil soluble silicon oil: alcohol = 1: 10~100 (in weight proportion). The added amount of both solvents is 1~20% (in weight proportion) of the content of zinc oxide in

zinc-ammonia complex solution.

c. The said amphoteric coupling agent includes oil soluble and water soluble titanate coupler, or water soluble silane coupler, or water soluble aluminate coupler. The water soluble titanate coupler, or water soluble silane coupler, or aluminate coupler is prepared in the following ratio: water soluble titanate, or water soluble silane, or aluminate: water = 1: 1-2- (in weight proportion). The added amount of the solvent is 2-20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The oil soluble titanate coupler is prepared in the following ratio: oil soluble titanate: alcohol = 1: 1-20 (in weight proportion). The added amount of the solvent is 1-20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. /7

Instruction

Modified Microfine Zinc Oxide and Its Preparation

A. Technical Field

This invention concerns a nanometer and sub-micron modified microfine zinc oxide and its preparation method. The invention uses nanometer material production technique by applying some modifying solvents for modification preparation of microfine zinc oxide in order

to obtain high performance and high dispersivity modified microfine zinc oxide. This invention also provides a method for the preparation of modified microfine zinc oxide.

B. Background Technology

Microfine zinc oxide powder refers to powder with the particle diameter less than $1\mu\text{m}$. It is broadly applied in rubber, ceramic, textile, and general chemical industries. With decrease of particle diameter, the specific surface area of zinc oxide powder gradually increases, showing active effect not possessed by conventional powder. When the particle diameter is at nanometer level of less than 100nm , in particular, the quantum dimensional effect, surface effect, and small dimensional effect enable zinc oxide to have properties not possessed by conventional materials, such as optical, electronic, biological, and chemical properties. However, because the particle diameter of microfine powder is small and the specific surface area and surface energy are very large, it is easy for the particles to agglomerate, which will greatly impede the full elaboration of the performance of microfine powder. Therefore, it is necessary to study the dispersivity and stability of microfine powder so as to further improve the performance of powder material. In addition, in order to improve the optical, electronic, biological, and chemical

properties of microfine zinc oxide, the powder surface is usually modified for the purpose of enhancing and stabilizing the dispersion property of microfine zinc oxide powder, and thus obtaining high performance microfine zinc oxide powder. The technical focus of this invention is to add different kinds of surface modifying solvents in the process of ammonia preparation of microfine zinc oxide or/and in the prepared microfine zinc oxide in order to obtain good dispersivity, good compatibility, and high functionality microfine zinc oxide. Different surface modifying solvents determine not only the dispersivity of the zinc oxide powder, but also the powder properties after modification. In this technical field, the 8 references retrieved include Germany patent DE19907704, which concerns the preparation of nanometer zinc oxide with the particle diameter less than 10nm. The patent applied hydrolytic decomposition process with addition of surface modifying solvent, making nanometer zinc oxide disperse evenly in organic phase or water phase. The Chinese Patent No. 95117887.3 entitled "Particle-shaped High Activity Zinc Oxide" applied active zinc oxide with addition of certain amount of surface modifying solvent to prepare particle-shaped high activity zinc oxide in good dispersivity. Compared to the above two patents, this invention: a. has different zinc oxide preparation process; b.

uses different types of surface modifying solvents; and c. applies different method for the preparation of modified zinc oxide powder. The microfine zinc oxide preparation process used in this invention comes from Chinese Patent ZL 98.1 16820.5 entitled "Technical Process for Alkaline Production of Active Zinc Oxide", which refers to ammonia method for the preparation of large specific surface area microfine zinc oxide in order to obtain higher functionality modified microfine zinc oxide powder.

C. Content of Invention

The concept of this invention is to use surface modifying solvents with specific structures to generate space steric effect between zinc oxide particles, and to alter electrostatic repulsion effect generated by the potential on the particle surface in order to disperse zinc oxide and improve the performance of zinc oxide. These surface modifying solvents can not only disperse zinc oxide, but also improve the properties of zinc oxide after modification.

Therefore, the objective of this invention is to provide the public with a patent technique on the modified nanometer and sub-micron microfine zinc oxide and its preparation method.

The technical contents of this invention include a technical solution on the modified microfine zinc oxide, and a technical

solution on the preparation of microfine zinc oxide. The preparation method includes wet preparation, dry preparation, and wet-dry combined preparation.

The specific contents of the technical solutions of this invention are as follows:

The modified microfine zinc oxide is nanometer and sub-micron microfine zinc oxide. In the ammonia evaporation process for the alkaline preparation of microfine zinc oxide or/and after preparation of microfine zinc oxide, modifying solvent is added in the zinc oxide and appropriate modification process and method, such as impurity removal, purification, drying, and burning after ammonia evaporation,

/9

are applied to modify microfine zinc oxide in order to obtain high performance, multi-functional, modified nanometer and sub-micron microfine zinc oxide. The modifying solvent added in the modification preparation process can be surface modifier, or new polymer super dispersant, or amphoteric coupling agent. The amount of each modifying solvent added is 0.1~20% of the content of zinc oxide (in weight proportion).

The preparation of the above-mentioned modified microfine zinc oxide includes the following specific technical content: The

modifying solvent added in the modification preparation is one of two kinds of the following modifying solvents, whereas the amount of each modifying solvent added or the total amount of two kinds of modifying solvents added accounts for 0.1~20% of the content of zinc oxide (in weight proportion); a. The surface active agent of modifying solvent added in the modification preparation process is anion surface active agent and non-ionic surface active agent, whereas the anion surface active agent includes C_{12-18} aliphatic acid and its salt, alkylbenzene sulfonate, alkyl ether organic phosphate, and alcohol ether carboxylate, whereas non-ionic surface active agent includes polyethylene (the molecular weight is $\overline{M}=200-20000$) and fatty alcohol polyoxyethylene ether; The C_{12-18} aliphatic acid refers to aliphatic acid containing 12~18 carbon atoms in each molecule. The polyethylene includes all polyethylene compounds with the average molecular weight \overline{M} value of 200-20000; b. The new polymer super dispersant of modifying solvent added in the modification preparation process is polyacrylate, and water soluble and oil soluble silicon oil; c. The amphoteric coupling agent of modifying solvent added in the modification preparation process is silane coupler, titanate coupler, and aluminate coupler, whereas titanate coupler includes water soluble and oil soluble titanate coupler.

The preparation of the above-mentioned modified microfine zinc oxide includes the following more specific technical content: a. The added amount of ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, and alcohol ether carboxylate (0.1~1mol/L) serving as the said anion surface active agent is 0.5~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution, while the added amount of water soluble stearic acid (0.1~1mol/L) is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; The added amount of polyethylene or fatty alcohol polyoxyethylene ether (0.1~1mol/L)

/10

serving as non-ionic surface active agent is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; b. The said polyacrylate serving as a polymer super dispersant is a water solvent prepared in the following ratio: polyacrylate: water = 1: 10~100 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The water soluble silicon oil is prepared in the following ratio: water soluble silicon oil: water = 1: 10~100 (in weight proportion). The oil soluble silicon oil is prepared in the following ratio: oil soluble silicon oil:

alcohol = 1: 10~100 (in weight proportion). The added amount of both solvents is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. c. The said amphoteric coupling agent includes oil soluble and water soluble titanate coupler, or water soluble silane coupler, or water soluble aluminate coupler. The water soluble titanate coupler, or water soluble silane coupler, or aluminate coupler is prepared in the following ratio: water soluble titanate, or water soluble silane, or aluminate: water = 1: 1~2- (in weight proportion). The added amount of the solvent is 2~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The oil soluble titanate coupler is prepared in the following ratio: oil soluble titanate: alcohol = 1: 1~20 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. It is necessary to point out that the water used by the above water soluble solvent and organic solvent used by water soluble solvent must be pure and clean.

The method for the preparation of modified microfine zinc oxide refers to the method for the preparation of nanometer and sub-micron modified microfine zinc oxide by adding modifying solvent during the ammonia evaporation process of alkaline preparation of microfine zinc

oxide or/and in the prepared microfine zinc oxide. This preparation method enables microfine zinc oxide to alter its properties, improve or enhance its functionality. In the said preparation method, the process known to the public includes the formation of zinc-ammonia complex solution with zinc oxide, carbon-ammonium, and ammonia water in fixed proportion, as well as ammonia evaporation, impurity removal, purification, drying, and burning steps. The technical essentials of the method are: 1. In the said preparation method, the added modifying solve is surface active agent, or new polymer super dispersant, or amphoteric coupling agent; 2. The method for the preparation of modified microfine zinc oxide includes operating steps and processes of wet preparation, dry preparation, or wet-dry combined preparation, whereas: a. The operating steps and processes of wet

/11

preparation of modified microfine zinc oxide include: (1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use; (2) In the ammonia evaporation process of alkaline preparation of microfine zinc oxide, add water soluble or oil soluble modifying solvent at normal temperature and pressure in the zinc-ammonia complex solution in the ammonia evaporation equipment in the amount of 0.1~20%

(in weight proportion) of content of zinc oxide in zinc-ammonia complex solution, and then stir the solution, increase temperature, evaporate ammonia, stop ammonia evaporation when the ammonia content in the solution is less than 5% (in weight proportion), and conduct follow-up processes to obtain modified microfine zinc oxide powder to test and store for later use; b. The operating steps and processes of dry preparation of modified microfine zinc oxide include: (1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use; (2) Place microfine zinc oxide powder made from alkaline preparation process in the preparation equipment. Stir, increase temperature, and add water soluble modifying solvent. Increase temperature to 100~110°C. Upon finishing addition of modifying solvent, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. The amount of added modifying solvent is 0.1~20% (in weight proportion) of the content of zinc oxide. While adding oil soluble modifying solvent, it is necessary to stir dry zinc oxide powder in the preparation equipment, increase temperature and add oil soluble modifying solvent. Upon finishing addition of modifying solvent, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. The amount of modifying solvent added is 0.1~20%

(in weight proportion) of the content of zinc oxide; (3) Take out the modified microfine zinc oxide powder obtained from dry preparation to test and store for later use; c. The operating steps and processes of wet-dry combined preparation of modified microfine zinc oxide include: (1) First dissolve water soluble modifying solvent in water, or dissolve oil soluble modifying solvent in a water soluble organic solvent for later use; The total amount of one modifying solvent added in two times or two modifying solvents altogether is 0.1~20% of the content of zinc oxide. (2) In the ammonia evaporation process of alkaline preparation of microfine zinc oxide, add water soluble or oil soluble modifying solvent at normal temperature and pressure in the zinc-ammonia complex solution in the ammonia evaporation equipment, stir the solution, increase temperature, evaporate ammonia, stop ammonia evaporation when the ammonia content in the solution is less than 5% (in weight proportion), and then conduct follow-up processes to obtain modified microfine zinc oxide powder. After that, apply dry preparation method. (3) Take modified microfine zinc oxide powder obtained from wet preparation and place the modified zinc oxide dry powder in the preparation equipment. Stir the solution, increase

/12

temperature, and add in water soluble modifying solvent. When the

temperature increases to 100~110°C, keep the temperature constant and stir the zinc oxide powder for 30~60 minutes. While adding oil soluble modifying solvent, it is necessary to first stir the dry zinc oxide powder in the preparation equipment, increase temperature, and add in oil soluble modifying solvent. Upon finishing addition of modifying solvent, keep the temperature constant and stir zinc oxide powder for 30~60 minutes; (4) Take out the modified microfine zinc oxide powder prepared through wet-dry combine methods to test and store for later use.

The preparation of the above-mentioned modified microfine zinc oxide includes the following specific technical content: The modifying solvent added in the modification preparation is one of two kinds of the following modifying solvents, whereas the amount of each modifying solvent added or the total amount of two kinds of modifying solvents added accounts for 0.1~20% of the content of zinc oxide (in weight proportion); a. The surface active agent of modifying solvent added in the modification preparation process is anion surface active agent and non-ionic surface active agent, whereas the anion surface active agent includes C_{12-18} aliphatic acid and its salt, alkylbenzene sulfonate, alkyl ether organic phosphate, and alcohol ether carboxylate, whereas non-ionic surface active agent includes

polyethylene (the molecular weight is $M=200-20000$) and fatty alcohol polyoxyethylene ether; The C_{12-18} aliphatic acid refers to aliphatic acid containing 12~18 carbon atoms in each molecule. The polyethylene includes all polyethylene compounds with the average molecular weight M value of 200-20000; b. The new polymer super dispersant of modifying solvent added in the modification preparation process is polyacrylate, and water soluble and oil soluble silicon oil; c. The amphoteric coupling agent of modifying solvent added in the modification preparation process is silane coupler, titanate coupler, and aluminate coupler, whereas titanate coupler includes water soluble and oil soluble titanate coupler.

The preparation of the above-mentioned modified microfine zinc oxide includes the following more specific technical content: a. The added amount of ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, and alcohol ether carboxylate ($0.1\sim 1\text{mol/L}$) serving as the said anion surface active agent is 0.5-15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution, while the added amount of water soluble stearic acid ($0.1\sim 1\text{mol/L}$) is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; The added amount of polyethylene or fatty alcohol polyoxyethylene ether ($0.1\sim 1\text{mol/L}$)

serving as non-ionic surface active agent is 1~15% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; b. The said polyacrylate serving as a polymer super dispersant is a water solvent prepared in the following ratio: polyacrylate: water = 1: 10~100 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. The water soluble silicon oil is prepared in the following ratio: water soluble silicon oil: water = 1: 10~100 (in weight proportion). The oil soluble silicon oil is prepared in the following ratio: oil soluble silicon oil: alcohol = 1: 10~100 (in weight proportion). The added amount of both solvents is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution; c. The said amphoteric coupling agent includes oil soluble and water soluble titanate coupler, or water soluble silane coupler, or water soluble aluminate coupler. The water soluble titanate coupler, or water soluble silane coupler, or aluminate coupler is prepared in the following ratio: water soluble titanate, or water soluble silane, or aluminate: water = 1: 1~2- (in weight proportion). The added amount of the solvent is 2~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex

solution. The oil soluble titanate coupler is prepared in the following ratio: oil soluble titanate: alcohol = 1: 1~20 (in weight proportion). The added amount of the solvent is 1~20% (in weight proportion) of the content of zinc oxide in zinc-ammonia complex solution. As mentioned above, the water used by the above water soluble solvent and organic solvent used by water soluble solvent must be pure and clean.

The various modified microfine zinc oxide prepared through addition of different modifying solvents as described in the above method are tested by relevant inspection agency using 100,000-magnitude transmission electron microscope that the zinc oxide particles have reached nanometer and sub-micron level.

The modified nanometer and sub-micron microfine zinc oxide and its preparation method as described in this invention have many advantages. First, by adding small amount of modifying solvents, this preparation method takes advantage of the space steric effect of surface active agent to effectively control the size of zinc oxide so as to obtain good dispersivity and highly functional modified microfine zinc oxide. Secondly, the applied modification preparation method is established on zinc oxide preparation method such as ammonia evaporation process, simple dry preparation operation, or wet-dry

combined preparation, thus resulting in better properties of modified zinc oxide. In conclusion, this preparation method is easy to operate,

/14

cost-effective, practical, and thus worth to be popularized. The modified microfine zinc oxide powder can be broadly applied in rubber, ceramic, textile, and general chemical industries.

D. Illustrations of Attached Figures

There is 1 attached figure in this invention.

Fig. 1 shows the process flow of the method for the preparation of modified microfine zinc oxide;

In Fig. 1, 1 represents different modifying solvents; 2 represents wet preparation flow; 3 represents zinc-ammonia complex solution; 4 represents ammonia evaporation; 5 represents impurity removal; 6 represents purification; 7 represents drying; 8 represents burning; 9 represents modified microfine zinc oxide made by wet preparation method; 10 represents dry preparation flow; 11 represents microfine zinc oxide made by ammonia method; 12 represents stirring; 13 represents modified microfine zinc oxide made by dry preparation method; 14 represents wet-dry combined preparation flow; 15 represents modified microfine zinc oxide made by wet-dry combined preparation method.

E. Implementations

Implementation 1

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies wet method to prepare modified microfine zinc oxide in the following steps: Use C_{16-18} ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, or alcohol ether carboxylate to prepare 0.1mol/L, or 0.5mol/L, or 0.8mol/L, or 1mol/L modifying solvent; Add modifying solvent in the zinc-ammonia complex solution in the ammonia evaporation equipment. The content of ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, or alcohol ether carboxylate modifying solvent accounts for 0.5%, or 5%, or 15%, or 20% that of zinc oxide (in weight proportion); Stir the solution after addition of modifier to increase temperature; Keep temperature constant when the temperature increases to 80~90°C to evaporate ammonia; Stop ammonia evaporation when the ammonia content is less than 5% (in weight proportion); Conduct deposition, impurity removal, purification, drying, burning processes to obtain modified microfine zinc oxide powder.

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, anion surface modifying solvent such as C₁₆₋₁₈ ammonium stearate, or alkylbenzene sulfonate, or alkyl ether organic phosphate, or alcohol ether carboxylate is added for modification preparation of microfine zinc oxide. The amount of

/15

modifying solvent added accounts for 0.5%, or 5%, or 15%, or 20% (in weight proportion) the content of zinc oxide. The prepared modified microfine zinc oxide is observed using an H-600 transmission electron microscope and shown to have good dispersivity.

Implementation 2

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies wet method to prepare modified microfine zinc oxide in the following steps: Dissolve polyethylene (M=400) or fatty alcohol polyoxyethylene ether in a given amount of deionized water to prepare 0.2mol/L, or 0.5mol/L, or 0.7mol/L additive solution; Weigh polyethylene solution or fatty alcohol polyoxyethylene ether solution in the amount equivalent to 2%, or 4%, or 10%, or 18% (in weight proportion) the content of zinc oxide in zinc-ammonia complex solution and add the solution into the zinc-ammonia complex solution in the ammonia evaporation equipment;

Follow the rest steps identical to those described in Implementation 1 to obtain modified microfine zinc oxide powder.

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, non-ionic surface modifying solvent such as polyethylene or fatty alcohol polyoxyethylene ether is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 2%, or 4%, or 10%, or 18% (in weight proportion) the content of zinc oxide. The prepared modified microfine zinc oxide is observed using an H-600 transmission electron microscope and shown to have good dispersivity.

Implementation 3

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies wet method to prepare modified microfine zinc oxide in the following steps: Dissolve water soluble titanate coupler, or silane coupler, or aluminate coupler in a given amount of ionized water to prepare certain concentration of titanate (or silane, or aluminate) water solvent in the weight proportion of titanate (or silane, or aluminate): water = 1:10 (or 1:1, or 1:5, or 1:20); Take titanate, or silane, or aluminate solvent in the amount equivalent to 0.1%, or 2%, or 6%, or 10%, or 20% (in weight proportion)

the content of zinc oxide in zinc-ammonia complex solution and add the solvent into the zinc-ammonia complex solution in the ammonia evaporation equipment; Follow the rest steps identical to those described in Implementation 1 to obtain modified microfine zinc oxide powder.

/16

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, water soluble coupling agent such as titanate, or silane, or aluminate is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 0.1%, or 2%, or 6%, or 10%, or 20% (in weight proportion) the content of zinc oxide. The prepared modified microfine zinc oxide is tested to show good dispersivity.

Implementation 4

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies wet method to prepare modified microfine zinc oxide in the following steps: Dissolve polyacrylate or water soluble silicon oil in deionized water in the ratio of polyacrylate (or silicon oil): water = 1:100 (or 1:10, or 1:30, or 1:50, or 1:80) in the amount equivalent to 1%, or 4%, or 10%, or 20% (in weight proportion) the content of zinc oxide in zinc-ammonia

complex solution and add the solution into the zinc-ammonia complex solution in the ammonia evaporation equipment; Follow the rest steps identical to those described in Implementation 1 to obtain modified microfine zinc oxide powder.

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, polymer super dispersant such as polyacrylate or silicon oil is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 1%, or 4%, or 10%, or 20% (in weight proportion) the content of zinc oxide. The prepared modified microfine zinc oxide is observed using an H-600 transmission electron microscope and shown to have good dispersivity.

Implementation 5

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies dry method to prepare modified microfine zinc oxide in the following steps: Place prepared microfine zinc oxide powder in the preparation equipment; Take oil soluble titanate and dissolve it in a given amount of alcohol solvent in the ratio of titanate: alcohol = 1:10 (or 1:1, or 1:5, or 1:20) (in weight proportion); Weigh oil soluble titanate in the amount equivalent to

2%, or 8%, or 14%, or 20% the weight of zinc oxide powder and start stirring to increase temperature; Add titanate solution into the zinc oxide powder and control the temperature at 80~90°C; Keep the temperature constant upon finishing addition of the solution and keep stirring for 30 minutes to obtain dry modified microfine zinc oxide powder.

/17

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, oil soluble titanate is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 2%, or 8%, or 14%, or 20% (in weight proportion) the content of zinc oxide. The prepared modified microfine zinc oxide is tested to show good dispersivity.

Implementation 6

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies dry method to prepare modified microfine zinc oxide in the following steps: Place prepared microfine zinc oxide powder in the preparation equipment; Dissolve C_{12-16} ammonium stearate, or alkylbenzene sulfonate, or polyethylene, or polyacrylate, or water soluble titanate, or water soluble alluminate in a given amount of deionized water. The preparation of these solvents

is the same as described in the above implementations. Take prepared additive solvent in the amount equivalent to 0.1%, or 5%, or 10%, or 15%, or 19% (in weight proportion) the content of zinc oxide powder and start stirring to increase temperature; Add C₁₂₋₁₆ ammonium stearate solution, or alkylbenzene sulfonate solution, or polyethylene solution, or polyacrylate solution, or water soluble titanate solution, or water soluble alluminate solution in the zinc oxide dry powder and control the temperature at 105~110°C; Keep the temperature constant upon finishing addition of the solution and keep stirring for 40 minutes to obtain dry modified microfine zinc oxide powder.

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, C₁₂₋₁₆ ammonium stearate, or alkylbenzene sulfonate, or polyethylene, or polyacrylate, or water soluble titanate, or water soluble alluminate is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 0.1%, or 5%, or 10%, or 15%, or 19% (in weight proportion) the content of zinc oxide. The test result shows that the powder has certain dispersivity.

Implementation 7

(1) Method for the preparation of modified nanometer and

sub-micron microfine zinc oxide:

This implementation applies wet-dry combined method to prepare modified microfine zinc oxide in the following steps: Follow the steps in Implementations 1, 2, 3, 4 to obtain wet method modified microfine zinc oxide powders; Place the above modified powders in a dry method preparation equipment; Dissolve alkyl ether organic phosphate, or alcohol ether carboxylate, or fatty alcohol polyoxyethylene ether, or water soluble silicon oil, or water soluble titanate, or water soluble silane in a given amount of deionized water. The preparation ratio is as follows: each modifying solvent: water = 1:10 (or 1:1, or 1:5, or 1:20) (in weight proportion); Take prepared modifying solvent in the amount equivalent to 1%, or 6%, or 11%, or 17% (in weight proportion) the content of zinc oxide and start stirring to increase temperature; Add the above modifying solvents to wet method modified zinc oxide powder and increase the temperature to 100-110°C; Keep the temperature constant and keep stirring for 50 minutes to obtain various modified microfine zinc oxide powders from wet-dry combined method. It is necessary to point out that the total amount of modifying solvents added twice in wet method and dry method shall be 0.1-20% of the content of zinc oxide (in weight proportion).

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, alkyl ether organic phosphate, or alcohol ether carboxylate, or fatty alcohol polyoxyethylene ether, or water soluble silicon oil, or water soluble titanate, or water soluble silane is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 1%, or 6%, or 11%, or 17% (in weight proportion) the content of zinc oxide. The test result shows that the powder has very good dispersivity.

Implementation 8

(1) Method for the preparation of modified nanometer and sub-micron microfine zinc oxide:

This implementation applies wet-dry combined method to prepare modified microfine zinc oxide in the following steps: Follow the steps in Implementations 1, 2, 3, 4 to obtain wet method modified microfine zinc oxide powders; Place the above modified powders in a dry method preparation equipment; Dissolve oil soluble silicon oil, or oil soluble titanate in a given amount of alcohol solvent. The preparation ratio is as follows: silicon oil (or titanate): alcohol = 1:10 (or 1:1, or 1:5) (in weight proportion); The amount of modifying solvents added accounts for 0.5%, or 7%, or 13%, or 19% the content of zinc oxide (in weight proportion); Stir the modifying solvent and add it into wet method prepared zinc oxide powder. Keep the temperature

constant at 80~90°C and stir for 60 minutes; Follow the steps as described in Implementation 5 to obtain various modified microfine zinc oxide powders from wet-dry combined method. It is necessary to point out that the total amount of modifying solvents added twice in wet method and dry method shall be 0.1~20% of the content of zinc oxide (in weight proportion).

(2) Modified nanometer and sub-micron microfine zinc oxide:

In this implementation, new polymer super dispersant--oil soluble silicon oil, or coupling agent--oil soluble titanate is added for modification preparation of microfine zinc oxide. The amount of modifying solvent added accounts for 0.5%, or 7%, or 13%, or 19% (in weight proportion) the content of zinc oxide. The test result shows that the powder has very good dispersivity.

/20

Fig. 1

